NOTES

Effect of KBr on the micellar properties of CTAB

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Abstract The effect of KBr on the size, shape and microviscosity of CTAB micelles has been investigated by means of laser light scattering (LLS), ^{1}H NMR measurements and fluorescence probe. The data obtained from the various techniques are quantitatively in agreement. The R_h of micelles in 0.01 mol • L^{-1} CTAB solution increases from 3.5 nm to 43 nm and R_g increases to 89 nm with addition of KBr salt. In this process, both the microviscosity and molecular weight of micelles M_w have noticeable increases, too. The rod-like micelles are formed at 0.1 mol • L^{-1} KBr and the worm-like micelles are formed at above 0.2 mol • L^{-1} KBr.

Keywords: molar weight of micelle, radius of gyration, hydrodynamic radius, sphere-rod transition.

Recently, the size and structure of ionic micelles in the presence of additives have been extensively studied. For most aqueous ionic surfactant solutions just above the critical micelle concentration (CMC), the micelles are regarded as spherical in shape[1]. On the other hand, the deviation from spherical shape will happen at high surfactant concentration[2]. There is now very strong evidence for an entangled micellar phase in several aqueous cationic detergent systems in the presence of added salt, such as cetyltrimethylammonium bromide (CTAB) with added KBr or sodium salicylate (NaSal), cetylpridinium chloride (CpyCl)+KBr, cetylpridinium salicylate (CpySal)+NaSal, etc.[3—7]. It was found that the M_w of these micelles increases to 10^6 and the length grows to several hundreds of nm. However, there was relatively little work on the effect of the salt on the micellar properties of these systems. In this note we show the influence of KBr salt on the shape and size of micelles in the dilute CTAB solution. These results obtained from LLS, fluorescence probe and ^{1}H NMR spectra of CTAB molecules in micelles are quantitatively consistent.

1 Experimental

All of reagents in this study were of analysis reagent grade. Water was doubly distilled.

A commerical laser light scattering spectrometer (ALV/SP-150) equipped with a solid-state laser (ADLAS DPY425II, output power≈400 mW at λ = 532 nm) as the light source and an ALV-5000 multi-τ digital correlator were used. The samples were filtered through a 0.5 μm Millipore filter into the cylindrical light scattering cell[8,9].

The specific refractive index increment (dn/dc) used in static light scattering was determined by a novel and precise differential refractometer[8,9].

^{1}H NMR spectra were recorded using a Varian Unity Inova-300 instrument. The ^{1}H chemical shifts are reported in δ units (ppm) relative to tetramethylsilane (TMS) as external standard (δ = 0.00).

All measurements were conducted at the temperature of (30±0.5)℃.

2 Results and discussion

(i) Effect of KBr salt on ^{1}H NMR of CTAB molecules in 0.01 mol • L^{-1} CTAB solution. Fig. 1 illustrates the effect of KBr salt on the ^{1}H NMR of CTAB molecules in 0.01 mol • L^{-1} CTAB solution. The ^{1}H NMR bands start to broaden and the signals from the long chain methylenes of CTAB molecules become unresolved at KBr concentrations just above 0.1 mol • L^{-1}. The interpretation is that the surfactant molecules in micelles are mobile and free to rotate, causing a long longitudinal relaxation time and sharpening of signals with lower KBr salt content. When KBr concentration is more than 0.1 mol • L^{-1}, the mobility of CTAB molecules in micelles becomes weak and the longitudinal relaxation

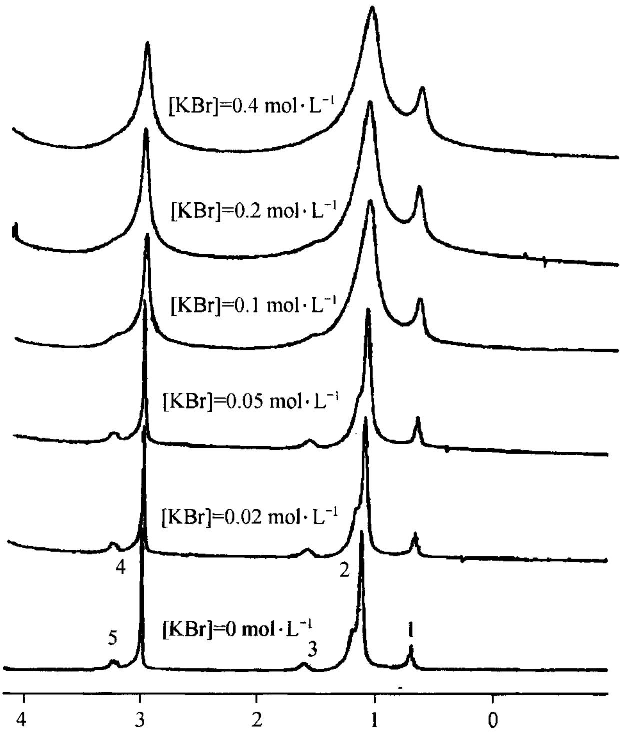

Fig. 1. Effect of KBr salt concentration on the ^{1}H NMR of CTAB molecules in the 0.01 mmol • L^{-1} micellar system. 1, ω-CH_3; 2, -$(CH_2)_{13}$; 3, β-CH_2; 4, N-$(CH_3)_3$; 5, α-CH_2.

time is short. Soltero[10] pointed out that broad ^{1}H NMR signals are typical of rod-like micelles. This implies that the arrangement of surfactant molecules in micelles becomes close and the rod micelles are formed at 0.1 mol • L^{-1} KBr.

(ii) Effect of KBr salt on R_g, R_h and M_w of CTAB micelles in 0.01 mol • L^{-1} CTAB solution. The light scattering data are given in table 1. Below 0.1 mol • L^{-1} KBr concentration, the exact values of R_g and M_w cannot be obtained due to the electrostatic interaction between the micelles, but the results of LLS show that M_w of CTAB micelles is in the order of 10^5 in 0.1 mol • L^{-1} KBr salt solution.

Table 1 Variance of R_g, R_h, M_w and R_g/R_h of micelles with KBr concentration in 0.01 mol • L^{-1} CTAB solutions

KBr/mol • L^{-1}	0	0.02	0.05	0.1	0.2	0.4	0.6
d*n*/d*c*				0.155	0.155	0.152	0.153
R_g/nm					43.19	70.36	89.46
R_h/nm	3.5	2.65	3.04	7.80	20.06	35.00	43.00
R_g/R_h					2.15	2.01	2.08
M_w				1×10^5	7.4×10^5	1.64×10^6	2.2×10^6

The rate of R_g/R_h is 0.775 for spheres and 2 for rigid rods according to theoretical prediction[4]. From table 1, the R_h of micelles retains a minimum value and the micelles should be sphere when KBr content is less than 0.1 mol • L^{-1}. At 0.1 mol • L^{-1} KBr, R_h increases abruptly to 7.8 nm and M_w is 10^5. This suggests that the micelle is rod. Above this salt concentration both R_h and R_g of micelles are more than 20 nm and R_g/R_h is more than 2. For the micelles of CTAB, the persistence length is about 20 nm[6]. These results show that in this stage, the micelles are worm-like.

(iii) Effect of KBr salt on the microviscosity of micelles in 0.01 mol • L^{-1} CTAB solution. Fluorescence probe pyrene is commonly solubilized in palisades of micelles[11]. The diffusion-limited pyrene monomer-excimer reaction would provide a way for measuring the microviscosity of the host micelle[12]. It is a common practice to use the I_E/I_M as a measure of microviscosity of micelles. The more the rate of I_E/I_M, the lower the microviscosity. In this study, the monomer emission I_M is observed at λ = 397 nm and that of excimer I_E at the wavelength of 470 nm. The effect of KBr salt on the I_E/I_M in 0.01 mol • L^{-1} CTAB micellar system is shown in fig. 2. Obviously, the microviscosity of micelle increases with addition of KBr salt.

It can also be seen from fig. 2 that above 0.1 mol • L^{-1} KBr, the velocity of increase in microviscosity of micelles becomes slow. This change suggests again that the arrangement of surfactant molecules in micelles is noticeable close.

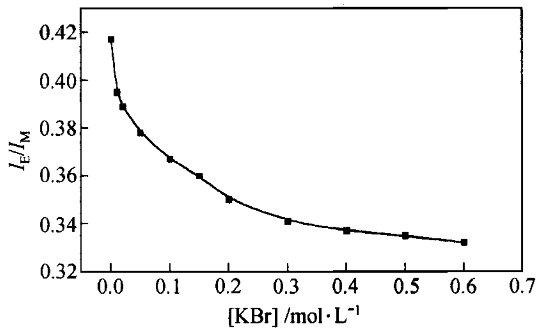

Fig. 2. The effect of KBr salt on the I_E/I_M of pyrene (1×10^{-4} mol • L^{-1}) in the 0.01 mol • L^{-1} CTAB micellar system.

Israelachvili et al.[13] have considered the geometric limitations which place restriction on allowed shapes of micelles. They gave a critical condition for the formation of rod micelles, i.e.

$$v / a_0 l_c > 1/3, \tag{1}$$

where l_c is roughly equal to but less than the fully extended length of the hydrocarbon chain of surfactant; a_0 is referred to as the optimal surface area per surfactant molecule, being that area where the free energy per surfactant molecule in a micelle is a minimum; v denotes the hydrocarbon chain volume per surfactant molecule in micelle.

In the CTAB micellar system, the addition of neutral salt decreases the electrostatic interaction between monomers in micelle and can bring about a decrease in a_0. In this process, v and l_c are almost constant. Once $v/a_0l_c > 1/3$, the rod micelles will be formed. With increasing continuously KBr content, the size of micelles grows steadily.

The results obtained in this study clearly show that below 0.1 mol • L^{-1} KBr concentration, the micelles in 0.01 mol • L^{-1} CTAB solution are sphere. When KBr content is above this concentration, the micelles transfer from rod micelles to worm-like ones. With addition of KBr salt, the microviscosity of micelles increases steadily.

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